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PATENT SPECIFICATION

NO DRAWINGS

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907,356



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91, D2(E:F:G:H:L:N:P:Q:V), S2(E:F:G:H:L:N:P:Q:V).

International Classification:—D06I. C11d.

The inventors of this invention in the sense of being the actual devisers thereof within the meaning of Section 16 of the Patents Act, 1949, are WILHELMUS JOHANNES CORNELIS VIVEEN and CORNELIS UGO KLOOSTERMAN, both of 13 Brink, Deventer, The Netherlands, both of Dutch nationality.

COMPLETE SPECIFICATION

Improvements in or relating to Washing and/or Bleaching
Compositions

ERRATA

SPECIFICATION No. 907,356

Page 1, line 11, for "This" read "The"
Page 1, line 49, for "positions" read "position"
Page 3, line 35, for "60°" read "65°"
Page 3, line 76, for "triplophosphate" read
"tripolyphosphate"
Page 5, line 46, for "13" read "12"
Page 12, line 38, for "non-ionic" read "non
ionic"
Page 12, line 69, and Page 21, line 19, for
"are" read "were"
Page 28, line 12, for "black currant" read
"blackcurrant"

THE PATENT OFFICE
2nd September 1963

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15
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25
IN the present context, the term "nitrile" includes natural and synthetic fibres, as well as products manufactured therefrom or there-with.

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35
It is well known, in washing and/or bleaching textiles, to make use of compositions containing, i.e., active oxygen releasing compounds having a bleaching effect on the textiles to be treated. As the active oxygen releasing compounds, inorganic peroxy compounds, e.g. inorganic persalts, such as perborates, percarbonates, perphosphates, persul-

60
65
70
At the same time, it is known that nitrile amide and compounds containing a nitrile group to washing compositions containing active oxygen releasing compounds. However, formamide is a liquid and is therefore difficult to incorporate into a washing powder. Also, the result obtained by adding formamide or nitriles is generally very slight.

It has now been found that if a compound containing one or more nitrogen atoms having at least two acyl groups attached to the same nitrogen atom or a mixture of such compounds

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9L, D2(E:F:G:H:L:N:P:Q:V), S2(E:F:G:H:L:N:P:Q:V).

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COMPLETE SPECIFICATION

Improvements in or relating to Washing and/or Bleaching Compositions

5 We, KONINKLIJKE INDUSTRIEEL MAAT-
SCHAPPIJ VOORHEEN NOURY & VAN DER
LANDE N.V., of 13 Brink, Deventer, The
Netherlands, a company organised and existing
under the laws of the Kingdom of the Nether-
lands, do hereby declare the invention, for
which we pray that a patent may be granted
to us, and the method by which it is to be
performed, to be particularly described in and
by the following statement:—

10 This invention relates to a process for the
preparation of a washing and/or bleaching
composition, which contains both an active
oxygen releasing compound as hereinafter
15 defined and an activator for this compound;
the invention also relates to a process for
washing and/or bleaching textiles with the aid
of a washing and/or bleaching liquid obtained
from the washing and/or bleaching composi-
20 tions according to the invention or with the
aid of a washing and/or bleaching liquid to
which one or more activators according to the
invention have been added.

25 In the present context, the term "textiles"
includes natural and synthetic fibres, as well
as products manufactured therefrom or there-
with.

30 It is well known, in washing and/or bleach-
ing textiles, to make use of compositions
containing, i.e., active oxygen releasing
compounds having a bleaching effect on the
textiles to be treated. As the active oxygen
releasing compounds, inorganic peroxy com-
35 pounds, e.g. inorganic persalts, such as per-
borates, percarbonates, perphosphates, persil-

icates and persulphates, and hydrogen peroxide
and sodium peroxide are used.

However, washing and/or bleaching com-
positions containing such active oxygen releas-
ing compounds generally have the disadvantage
40 that their bleaching effect is relatively low at
temperatures below 85° C., which gives rise
to difficulties when these compositions are used
in machines for household purposes in which
the temperature of the wash-water is not
45 higher than about 70° C.

It has already been proposed to enhance the
effect of a washing and/or bleaching com-
positions containing an active oxygen releasing
compound by adding thereto particular sub-
50 stances, so-called "activators." Definite quan-
tities of organic acid anhydrides, for instance,
have been added to washing and bleaching
compositions containing active oxygen releas-
ing compounds. However, in practice, this
55 measure does not yield the desired result, as
the activity of most acid anhydrides appears
to be insufficient in this respect.

It has also been proposed to add form-
amide and compounds containing a nitrile
group to washing compositions containing
active oxygen releasing compounds. However,
formamide is a liquid and is therefore difficult
60 to incorporate into a washing powder. Also,
the result obtained by adding formamide or
65 nitriles is generally very slight.

It has now been found that if a compound
containing one or more nitrogen atoms having
at least two acyl groups attached to the same
nitrogen atom or a mixture of such compounds
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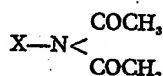
is added to a washing and/or bleaching composition containing an inorganic peroxy compound, a composition is obtained which is excellently suited to the washing and/or bleaching treatment of textiles at a temperature below boiling temperature.

Accordingly, one aspect of the invention consists in a process for preparing a washing and/or bleaching composition, which comprises adding to an inorganic peroxy compound an activator therefor comprising at least one compound containing one or more nitrogen atoms and having at least two acyl groups attached to the same nitrogen atom.

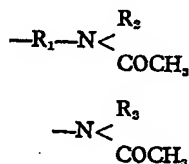
Another aspect of the invention consists in a process for washing and/or bleaching textile products, which comprises effecting washing and/or bleaching with the aid of a liquid containing an inorganic peroxy compound and an activator therefor comprising one or more compounds containing one or more nitrogen atoms and having at least two acyl groups attached to the same nitrogen atom.

A further aspect of the invention consists in a washing and/or bleaching composition comprising an inorganic peroxy compound and an activator therefor comprising at least one compound containing one or more nitrogen atoms having at least two acyl groups attached to the same nitrogen atom.

In a preferred embodiment of the invention, the activator is one or more compounds having the general formula:



in which X represents a phenyl radical, an acyl group derived from a lower aliphatic mono-carboxylic acid, a lower alkyl radical or a



group, in which R₁ represents a lower alkylene group and R₂ represents hydrogen or an acetyl group. In the present context, the term "lower" means a hydrocarbon group having 1 to 6 C atoms. Especially good results may be obtained if the activator is added in an amount corresponding to 0.5—4.0 bound acyl groups per atom of active oxygen.

The bleaching effect of the compositions according to the invention, when they are used at temperatures below boiling temperature and, especially, at temperatures between 15° and 85° C., is not only considerably better than the effect obtained at the same temperature

with compositions which do not contain an activator according to the invention, but furthermore is also greater than the effect obtained with hitherto known compositions at the boiling temperature. Moreover, the compositions according to the invention cause considerably less loss in strength of the fibres, practically do not chemically attack cellulose and synthetic fibres, such as polyamide fibres, and furthermore the disadvantages which arise from the use of the compositions hitherto known for washing coloured materials are practically fully eliminated, especially as regards attack on the colour, if for this purpose the compositions according to the invention are used. In addition, the compositions according to the invention are excellently suited to washing cotton goods, as such materials, even if washed several times, retain a high brightness and do not turn yellow. The bleaching compositions according to the invention and especially those containing perborate also possess the additional advantage that with a favourable ratio of perborate and activator an overbleaching is not possible. Furthermore, these bleaching compositions are excellently suited to addition to rinsing baths.

The following classes of compounds can be used as activators for oxygen releasing compounds in accordance with this invention: N-diacylated amines, e.g. diacetylmethylamine, diacetyl ethylamine, diacetylpropylamine, diacetylbutylamine, diacetylbenzylamine and diacetylaniline; N-diacylated ammonia, e.g. diacetamide, dipropionamide; N-diacylated amides, e.g. N-formyldiacetamide, N-acetyldiacetamide (triacetamide), N-propionyldiacetamide, N-butyryldiacetamide, N-valeryldiacetamide, N-caproyldiacetamide, N-acetylphthalimide, N-acetylsuccinimide, and N,N-diacetylcyanamide; N-diacylated urethanes, e.g. N,N-diacetylethylurethane and N-acetyl-N-propionylethylurethane; N-diacylated hydrazines, e.g. triacetylhydrazine, tetraacetylhydrazine, tripropionylhydrazine, N,N-diacetyl-N¹-benzoylhydrazine and N,N-diacetyl-N¹-isopropylidenehydrazine; N-diacylated alkylendiamines, e.g. N,N,N¹-triacetylmethylenediamine, N,N,N¹,N¹-tetra-acetylmethylenediamine, N,N,N¹,N¹-tetra-acetylene-diamine, tetra-acetylhexamethylenediamine and tetra-acetylphenylenediamine, and the N-diacyl derivatives of semicarbazide, thiosemicarbazide and dicyanodiamide.

The above-mentioned favourable properties of the washing and/or bleaching compositions according to the invention may be still further improved to a large extent, if the activator, as disclosed in co-pending Application No. 9441/62 (Serial No. 907,358), is coated with a solid material soluble in the washing and/or bleaching liquid.

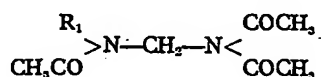
Washing and/or bleaching of textiles may be effected with the aid of a liquid containing

the compositions according to the invention.

However, it is also possible to execute this treatment with a washing and/or bleaching liquid containing an inorganic peroxy compound to which one or more activators according to the invention have been added.

In both cases, very good results are obtained at a treatment-temperature below boiling temperature, preferably at a temperature between 15° and 85° C.

The activators for the active oxygen releasing compound in the washing and/or bleaching composition are selected, in accordance with a preferred feature of the invention, from the hitherto unknown compounds having the general formula:



in which R_1 represents a hydrogen atom or a COCH_3 group.

These new compounds, or mixtures thereof, may be obtained in the manner disclosed in co-pending Application No. 32189/61 (Serial No. 907,357).

Thus, it is possible, according to a preferred embodiment of the invention disclosed in the aforesaid copending Application No. 32189/61 (Serial No. 907,357) to prepare $\text{N}_1\text{N}_2\text{N}_3\text{N}_4$ -tetraacetylmethylenediamine by allowing ketene to react with N_1N_2 -diacetylmethylenediamine in an inert solvent in the presence of an acid-reacting catalyst.

This reaction may be carried out in benzene as the inert solvent, at a temperature of 30°—80° C., preferably however at a temperature of 50°—60° C., in the presence of 0.5—3%, preferably 2%, by weight of *p*-toluene-

sulphonic acid as catalyst calculated on the N_1N_2 -diacetylmethylenediamine. The $\text{N}_1\text{N}_2\text{N}_3\text{N}_4$ -tetra-acetylmethylenediamine formed may be recovered from the reaction mixture in any conventional way.

According to another preferred embodiment of the invention, $\text{N}_1\text{N}_2\text{N}_3\text{N}_4$ -tetra-acetylmethylenediamine is obtained by acetylating N_1N_2 -diacetylmethylenediamine with the aid of acetic anhydride and immediately eliminating the acetic acid formed during the reaction, e.g. by distillation.

If the acetic acid liberated is not eliminated from the reaction mixture during the reaction between diacetylmethylenediamine and acetic anhydride, $\text{N}_1\text{N}_2\text{N}_3$ -triacetylmethylenediamine is mainly formed.

When only a part of the quantity of acetic acid which could theoretically be formed during the acetylation is eliminated from the reaction mixture, mixtures are obtained which appear to contain besides tetra-acetylmethylenediamine, triacetylmethylenediamine.

In order that the invention may be readily understood by those skilled in the art, the following specific Examples are given by way illustration:

EXAMPLE I

Pieces of cotton fabric were soiled with the juice of blackcurrants, by evenly applying to them 2.7 cc. of blackcurrant juice per 100 cm² of surface of cotton fabric by means of a brush. After being dried in the air, the brightness of the fabric was measured with a photoelectric remission meter. It was 29% of the brightness of magnesium oxide.

Part of the pieces of material was washed for 15 minutes at 60° in suds of the following composition:

| | |
|---|----------|
| Sodium salt of dodecyl benzene sulphonic acid | 0.85 g/l |
| Lauryl isopropanolamide | 0.10 g/l |
| Tetrasodium pyrophosphate | 0.75 g/l |
| Pentasodium tripolyphosphate | 0.60 g/l |
| Alkaline water-glass ($\text{Na}_2\text{O}/\text{SiO}_2 = \frac{1}{2}$) | 0.20 g/l |
| Na CMC (100%) | 0.04 g/l |
| Sodium sulphate | 0.80 g/l |
| Sodium perborate-tetrahydrate (10.2% active oxygen) | 0.50 g/l |

The percentage of brightness of the washed pieces of material amounted to 64 (brightness of magnesium oxide = 100 units), which is 13

units higher than the percentage of brightness of the pieces of material after thorough rinsing with water, which was 51.

Another part of the material was washed in suds of the same composition, to which respectively 0.1, 0.4 and 0.5 g/l of tetra-acetylhydrazine was added. These suds contained 5 per atom of active oxygen from the perborate 0.63, 2.50 and 3.14 acetyl groups as tetra-acetyl hydrazine, respectively.

The percentages of brightness of the thus-washed material were respectively 20, 31 and 10 34 units higher than the percentage of bright-

ness of the material which was only thoroughly rinsed with water. The relative improvements by adding tetra-acetylhydrazine in the concentrations mentioned were therefore 54%, 138% and 162%.

EXAMPLE II

Pieces of the same kind of fabric, soiled with blackcurrant juice, as used in Example I, were washed for 15 minutes at 60° C. in suds of the following composition:

| | |
|--|----------|
| Sodium soap | 3.1 g/l |
| Sodium carbonate | 1.00 g/l |
| Neutral Water-glass ($\text{Na}_2\text{O}/\text{SiO}_2 = 1/3.3$) | 0.17 g/l |
| Sodium perborate-tetrahydrate (9.9% of active oxygen) | 0.68 g/l |

The percentage of brightness of the material was increased to 62% by washing (brightness of magnesium oxide = 100 units); this is 11 units higher than the brightness obtained by only rinsing the material thoroughly with water.

If the suds also contained 0.42 g/l of tetra-acetyl hydrazine, the percentage of brightness of the material was increased to 73, which is 22 units more than the percentage of brightness obtained after thoroughly rinsing with

water only. The relative improvement by adding tetra-acetyl hydrazine therefore amounted to 100%. In this case, the number of acetyl groups added to the suds as tetra-acetyl hydrazine was 2.0 per atom of active oxygen from the perborate.

EXAMPLE III

A detergent in powder form had the following composition:

| |
|---|
| 20.0% of sodium salt of dodecyl-benzene sulphonic acid (the dodecyl group being derived from tetrapropylene) |
| 16.0% of tetrasodium pyrophosphate |
| 16.0% of pentasodium tripolyphosphate |
| 4.8% of neutral water-glass ($\text{Na}_2\text{O}/\text{SiO}_2 = 1/3.3$) |
| 2.0% of sodium salt of carboxymethylcellulose |
| 27.6% of sodium sulphate |
| 13.6% of water |
| 100.0% |

100 parts by weight of this powder were mixed with 8 parts by weight of sodium perborate-tetrahydrate and 6.25 parts by weight of tetra-acetyl hydrazine (STAH mixture).

A solution was prepared containing 5.70 g/l of the STAH mixture and pieces of the same kind of material stained with fruit juice, as used in Example I, were washed in this solu-

tion for 15 minutes at 60° C.

The material was then rinsed three times, ironed with a hot iron and the brightness was measured with a Hunter photoelectric remission meter.

Besides this test, a similar test was carried out with a mixture of 100 parts by weight of the afore-mentioned powder and 8 parts by weight of sodium perborate-tetrahydrate with-

out tetra-acetyl hydrazine (mixture SO). 5.4 grams per litre of solution were used of this mixture.

5 The brightness of the material washed with the STAII mixture was 27 units higher than the brightness of material only thoroughly rinsed with water (51 units).

10 In the case of the SO mixture, this difference in brightness was 12 units (brightness of magnesium oxide = 100 units).

By using a quantity of tetra-acetyl hydrazine corresponding to 2.5 bound acetyl groups per atom of active oxygen, a relative improvement of 125% was therefore obtained.

EXAMPLE IV

15 100 parts by weight of the powder described in Example III were mixed with 8 parts of sodium perborate-tetrahydrate and 6.60 parts of triacetyl hydrazine (STrAH mixture).

20 A solution was prepared containing 5.75 g per litre of this STrAH mixture and the same washing test was carried out with it as described in Example III.

25 The brightness of the material appears to be 22 units higher than the brightness of the material rinsed with water thoroughly (51 units). In the case of the SO mixture, this difference in brightness was 12 units.

30 The relative improvement in this case, where 2.5 bound acetyl groups per atom of active oxygen were used, was therefore 83%.

EXAMPLE V

35 100 parts by weight of the powder described in Example III were mixed with 8 parts of sodium perborate-tetrahydrate and 11.0 parts of tripropionyl hydrazine (STrPrH mixture).

40 A solution was prepared containing 5.95 g per litre of this STrPrH mixture and a similar washing test was carried out with it as described in Example III, except that in this case the experiment was carried out at 50° C.

45 The brightness of the washed material appeared to be 23 units higher than the brightness of material thoroughly rinsed with water (51 units). In the case of the SO mixture, this difference in brightness was 13 units.

The relative improvement in this case, where 3.3 bound propionyl groups per atom of active oxygen were used, was therefore 92%.

EXAMPLE VI

50 100 parts by weight of the powder described in Example III were mixed with 8 parts of sodium perborate-tetrahydrate and 7.05 parts of tetra-acetylenediamine (STAED mixture).

55 A solution was prepared containing 5.75 g per litre of this STAED mixture and a similar washing test was carried out with it as described in Example III, except that another lot of cotton fabric, soiled with blackcurrant juice, was used.

60 The brightness of the washed material appeared to be 23 units higher than the brightness of material rinsed thoroughly with water (51 units). In the case of the SO mixture, this

difference in brightness was 13 units.

The relative improvement in this case, where 2.5 bound acetyl groups per atom of active oxygen were used, was therefore 77%.

EXAMPLE VII

70 100 parts by weight of the powder described in Example III were mixed with 8 parts of sodium perborate-tetrahydrate and 6.31 parts of diacetamide (SDAA mixture).

75 A solution was prepared containing 5.72 g per litre of this SDAA mixture and a similar washing test was carried out with it as described in Example VI.

80 The brightness of the washed material appeared to be 22 units higher than the brightness of material rinsed thoroughly with water (51 units). In the case of the SO mixture, this difference in brightness was 13 units.

85 The relative improvement in this case, where 2.5 bound acetyl groups per atom of active oxygen were used, was therefore 69%.

EXAMPLE VIII

90 100 parts by weight of the powder described in Example III were mixed with 8 parts of sodium perborate-tetrahydrate and 5.96 parts of triacetamide (STrAA mixture).

A solution was prepared containing 5.70 g per litre of this STrAA mixture and a similar washing test was carried out with it as described in Example VI.

95 The brightness of the washed material appeared to be 30 units higher than the brightness of material rinsed thoroughly with water (51 units). In the case of the SO mixture, this difference in brightness was 13 units.

100 The relative improvement in this case, where 2.5 bound acetyl groups per atom of active oxygen were used, was therefore 131%.

EXAMPLE IX

105 A detergent in powder form had the following composition:

43% of sodium soap
25% of sodium carbonate
3% of neutral water-glass
29% of water
100%

110 100 parts by weight of this powder were mixed with 7.5 parts by weight of sodium perborate-tetrahydrate and 6.70 parts by weight of diacetylpropylamine (ZDAPrA mixture).

115 A solution was prepared containing 9.14 g per litre of this ZDAPrA mixture and pieces of the same kind of material soiled with fruit juice, as used in Example I, were washed in this solution for 15 minutes at 50° C.

120 The material was then rinsed three times, ironed with a hot iron and the brightness was measured with a Hunter photoelectric remission meter.

125 Besides this test, a similar test was carried out with a mixture of 100 parts by weight of the afore-mentioned powder and 7.5 parts by

weight of sodium perborate-tetrahydrate without diacetyl propylamine (ZO mixture), 8.60 grams per litre of this mixture were used.

5 The brightness of the material washed with the ZDAPrA mixture was 19 units higher than the brightness of material thoroughly rinsed with water only (51 units).

10 In the case of the ZO mixture, this difference in brightness was 12 units (brightness of magnesium oxide = 100 units).

By using a quantity of diacetyl propylamine corresponding to 2.0 bound acetyl groups per atom of active oxygen, a relative improvement of 58% was therefore obtained.

15 EXAMPLE X

100 parts by weight of the powder described in Example IX were mixed with 7.5 parts by weight of sodium-perborate-tetrahydrate and 6.55 parts by weight of diacetanilide (ZDAAL mixture).

20 A solution was prepared containing 9.30 g per litre of this ZDAAL mixture and a similar washing test was carried out with it as described in Example IX.

25 The brightness of the material washed with the ZDAAL mixture was 23 units higher than the brightness of material thoroughly rinsed with water (51 units). In the case of the ZO mixture, this difference in brightness was 12 units.

30 The relative improvement in this case, where 2.0 bound acetyl groups per atom of active oxygen were used, was therefore 92%.

35 EXAMPLE XI

A similar washing test to that described in Example I was carried out using suds contain-

ing 513 mg per litre N-ethyldiacetamide instead of tetra-acetyl hydrazine.

The relative improvement in the brightness of the washed material was 125% in this case, where 2.5 bound acetyl groups per atom of active oxygen were used.

EXAMPLE XII

4 A similar washing test to that described in Example II was carried out using suds containing 724 mg per litre N,N-diacetyl urethane instead of tetra-acetyl hydrazine.

5 The relative improvement in the brightness of the washed material was 41% in this case, where 2.0 bound acetyl groups per atom of active oxygen were used.

EXAMPLE XIII

5 A similar washing test to that described in Example I was carried out using suds containing 753 mg per litre N-acetyl phthalimide instead of tetra-acetyl hydrazine.

6 The relative improvement in the brightness of the washed material was 136% in this case, where 1.25 bound acetyl groups per atom of active oxygen were used.

EXAMPLE XIV

6 Pieces of cotton fabric were soiled as described in Example I. After drying in the air, rinsing thoroughly with water and drying again, the brightness of the pieces of fabric, measured with a photoelectric remission meter, was 53% of the brightness of magnesium oxide freshly condensed from the atmosphere.

7 Seven lots of these pieces of material were washed for 10 minutes at 60° C. in seven different suds.

All these suds contained:

| | |
|---|----------|
| Sodium salt of dodecyl benzene sulphonic acid | 0.85 g/l |
| Lauryl isopropanolamide | 0.10 g/l |
| Tetrasodium pyrophosphate | 0.75 g/l |
| Pentasodium tripolyphosphate | 0.60 g/l |
| Alkaline water-glass ($\text{Na}_2\text{O}/\text{SiO}_2 = \frac{1}{2}$) | 0.20 g/l |
| NaCMC (100%) | 0.04 g/l |
| Sodium sulphate | 0.80 g/l |

All concentrations refer to the anhydrous substances.

Further components of the different suds were as follows:

Suds 1: sodium perborate (10.0% active oxygen) 0.52 g/l

Suds 2: sodium perborate 0.50 g/l

N,N' -tetra-acetylmethylene-diamine 0.40 g/l
(hereinafter referred to as TAMD)

$$\text{ratio} \frac{\text{bound acetyl groups}}{\text{atoms active oxygen}} = 2.4$$

Suds 3: sodium perborate 0.40 g/l

TAMD 0.40 g/l

$$\text{ratio} \frac{\text{bound acetyl groups}}{\text{atoms active oxygen}} = 3.0$$

Suds 4: sodium perborate 0.40 g/l

TAMD 0.30 g/l

$$\text{ratio} \frac{\text{bound acetyl groups}}{\text{atoms active oxygen}} = 2.25$$

Suds 5: sodium perborate 0.30 g/l

TAMD 0.40 g/l

$$\text{ratio} \frac{\text{bound acetyl groups}}{\text{atoms active oxygen}} = 4.0$$

Suds 6: sodium perborate 0.30 g/l

TAMD 0.30 g/l

$$\text{ratio} \frac{\text{bound acetyl groups}}{\text{atoms active oxygen}} = 3.0$$

Suds 7: sodium perborate 0.20 g/l

TAMD 0.30 g/l

$$\text{ratio} \frac{\text{bound acetyl groups}}{\text{atoms active oxygen}} = 4.4$$

After washing, rinsing and drying the brightness of the pieces of material was measured.

The results were:

| Suds No. | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|---|----|------|------|------|------|------|------|
| Brightness (% of MgO) | 62 | 81 | 79 | 79 | 76 | 76 | 71.5 |
| Difference with the washing test without TAMD | 0 | 19 | 17 | 17 | 14 | 14 | 9.5 |
| Relative improvement | 0 | 210% | 190% | 190% | 155% | 155% | 105% |

5 The relative improvement is expressed as percentages of the difference in brightness between the pieces of material washed with 0.52 g/l perborate without TAMD and the pieces of material only rinsed with water (brightness 53).

10 In spite of the very considerable decrease in perborate content of some of the suds, great improvements in bleaching effect were obtained when TAMD was added to the suds.

EXAMPLE XV

A detergent in powder form was made up having the following composition:

50% of sodium soap
16% of sodium carbonate
3% of neutral water-glass
31% of water

15

Subsequently, five mixtures were prepared, namely:

Mixture 1: 90 parts by weight of the above-mentioned detergent
10 parts by weight of sodium perborate (9.7% active oxygen)

Mixture 2: 85.9 parts by weight of the above-mentioned detergent
3.6 parts by weight of sodium perborate
5.5 parts by weight of TAMD

$$\text{ratio } \frac{\text{bound acyl groups}}{\text{atoms active oxygen}} = 2.0$$

Mixture 3: 87.1 parts by weight of the above-mentioned detergent
8.7 parts by weight of sodium perborate
4.2 parts by weight of TAMD

$$\text{ratio } \frac{\text{bound acyl groups}}{\text{atoms active oxygen}} = 1.5$$

Mixture 4: 88.5 parts by weight of the above-mentioned detergent
5.8 parts by weight of sodium perborate
5.7 parts by weight of TAMD

$$\text{ratio } \frac{\text{bound acyl groups}}{\text{atoms active oxygen}} = 3.0$$

Mixture 5: 91.0 parts by weight of the above-mentioned detergent
4.6 parts by weight of sodium perborate
4.4 parts by weight of TAMD

$$\text{ratio } \frac{\text{bound acyl groups}}{\text{atoms active oxygen}} = 3.0$$

These mixtures were used in concentrations of 6.9, 7.2, 7.1, 7.0 and 6.8 g/l respectively.

In this way, the following concentrations were obtained (in g/l):

| Mixture No. | 1 | 2 | 3 | 4 | 5 |
|---------------------|------|------|------|------|------|
| Sodium soap | 3.1 | 3.1 | 3.1 | 3.1 | 3.1 |
| Sodium carbonate | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 |
| Neutral water-glass | 0.19 | 0.19 | 0.19 | 0.19 | 0.19 |
| Sodium perborate | 0.69 | 0.62 | 0.62 | 0.41 | 0.31 |
| TAMD | 0.0 | 0.40 | 0.30 | 0.40 | 0.30 |

Five lots of pieces of cotton material, soiled with the same blackcurrant juice as in Example XIV, were washed in these suds for 10 minutes at 60° C. After washing, rinsing and

drying, the brightness of the pieces of material was measured, which gave the following results:

| Mixture No. | 1 | 2 | 3 | 4 | 5 |
|---|------|------|------|------|------|
| Brightness (% of MgO) | 62.5 | 75 | 66.5 | 70 | 65.5 |
| Difference with the washing test without TAMD | 0 | 12.5 | 4.0 | 7.5 | 3.0 |
| Relative improvement | 0 | 208% | 67% | 125% | 50% |

10 The relative improvement is expressed as percentages of the difference in brightness between the pieces of material washed with 0.69 g/l of perborate without TAMD (mixture 1) and the pieces of material only rinsed with

15 water (brightness 56.5).
In spite of the very considerable decrease in perborate content of some of the suds, great improvements in bleaching effect were obtained when TAMD was added to the suds.

20 **EXAMPLE XVI**

Pieces of cotton fabric were soiled with the

juice of blackcurrants as described in Example I. After drying in the air, rinsing thoroughly with water and drying again, the brightness of the pieces of fabric, measured with a photo-

25

Two lots of these pieces of material were washed for 10 minutes at 60° C. in four different suds, prepared in the following way:

30

A detergent was made up having the following composition:

| | |
|---|-------|
| Sodium salt of dodecyl benzene sulphonic acid | 22.4% |
| Lauryl isopropanolamide | 2.6% |
| Tetrasodium pyrophosphate | 20.0% |
| Pentasodium tripolyphosphate | 15.8% |
| Alkaline water-glass ($\text{Na}_2\text{O}/\text{SiO}_2 = \frac{1}{2}$) | 5.1% |
| Sodium carboxymethylcellulose (NaCMC) (100%) | 1.0% |
| Sodium sulphate | 21.0% |
| Water | 12.1% |

Subsequently four mixtures were prepared, namely:

| | |
|------------|---|
| Mixture 1: | 85.5 parts by weight of the above-mentioned detergent 14.5 parts by weight of sodium pyrophosphate perhydrate (8.05% active oxygen) |
| Mixture 2: | 77.9 parts by weight of the above-mentioned detergent 13.2 parts by weight of sodium pyrophosphate perhydrate 8.9 parts by weight of TAMD |
| Mixture 3: | 91.2 parts by weight of the above-mentioned detergent 8.8 parts by weight of sodium percarbonate (14.6% active oxygen) |
| Mixture 4: | 82.7 parts by weight of the above-mentioned detergent 7.8 parts by weight of sodium percarbonate 9.5 parts by weight of TAMD |

These mixtures were used in concentrations of 4.45, 4.88, 4.16 and 4.59 g/l respectively. To each of the suds, a quantity of oxygen bleaching agent was added which corresponded to 52 mg/l of active oxygen.

All suds contained the components of the original detergent in the same concentrations.

For the TAMD-containing mixtures 2 and 4, the ratio was:

$$\frac{\text{bound acyl groups}}{\text{atoms active oxygen}} = 2.5$$

After washing, rinsing and drying, the brightness of the pieces of material was measured.

The results were:

15

| Mixture No. | 1 | 2 | 3 | 4 |
|---|--------------------------|--------------------------|--------------|--------------|
| Oxygen releasing substance | pyrophosphate perhydrate | pyrophosphate perhydrate | percarbonate | percarbonate |
| Addition | — | TAMD | — | TAMD |
| Brightness (% of MgO) | 62 | 80 | 61 | 79 |
| Difference with the washing test without TAMD | 0 | 18 | 0 | 18 |
| Relative improvement | 0 | 190% | 0 | 212% |

The relative improvement caused by TAMD is expressed as a percentage of the difference in brightness between the pieces of material washed with the mixture containing the same

oxygen bleaching agent without TAMD and the pieces of material only rinsed with water (brightness 52.5).

EXAMPLE XVII
A detergent in powder form had the following composition:

50.7% of sodium soap
16.1% of sodium carbonate
2.8% of neutral water-glass
30.4% of water

5

Subsequently four mixtures were prepared, namely:

-
- Mixture 1: 88 parts by weight of the above-mentioned detergent
12 parts by weight of sodium pyrophosphate perhydrate (8.1% active oxygen)
- Mixture 2: 82.6 parts by weight of the above-mentioned detergent
11.3 parts by weight of sodium pyrophosphate perhydrate
6.1 parts by weight of TAMD
- Mixture 3: 93 parts by weight of the above-mentioned detergent
7 parts by weight of sodium percarbonate (14.6% active oxygen)
- Mixture 4: 87 parts by weight of the above-mentioned detergent
6.6 parts by weight of sodium percarbonate
6.4 parts by weight of TAMD
-

- 10 For the TAMD-containing mixtures 2 and 4, the ratio was:

$$\frac{\text{bound acyl groups}}{\text{atoms active oxygen}} = 2.0$$

- 15 These mixtures were used in concentrations of 6.9, 7.35, 6.53 and 6.98 g/l respectively. To each of the suds, a quantity of oxygen bleaching agent was added which corresponded

to 67 mg/l active oxygen.

All suds contained the components of the original detergent in the same concentrations.

Four lots of pieces of cotton material stained with the same blackcurrant juice as described in Example I were washed in these suds for 10 minutes at 60° C. After washing, rinsing and drying, the brightness of the pieces of material was measured, which gave the following results:

20

25

| Mixture No. | 1 | 2 | 3 | 4 |
|---|--------------------------|--------------------------|--------------|--------------|
| Oxygen releasing substance | pyrophosphate perhydrate | pyrophosphate perhydrate | percarbonate | percarbonate |
| Addition | — | TAMD | — | TAMD |
| Brightness (% of MgO) | 62 | 78 | 60.5 | 73 |
| Difference with the washing test without TAMD | 0 | 16 | 0 | 12.5 |
| Relative improvement | 0 | 200% | 0 | 192% |

5 The relative improvement caused by TAMD is expressed as percentages of the difference in brightness between the pieces of material washed with the mixture containing the same oxygen bleaching agent without TAMD and the pieces of material only rinsed with water (brightness 54).

EXAMPLE XVIII

10 Three comparative washing tests, similar to those described in Example I, were carried out using suds containing 0.39 g per litre sodium perborate (10.2% active oxygen), instead of 0.50 g per litre, and containing per litre respectively 335 mg tetra-acetyl methylenediamine, 358 mg triacetyl methylenediamine and 342 mg of a mixture of these compounds containing 67% tetra-acetyl methylenediamine.

15 The relative improvements in the brightness of the washed material were respectively 186%, 83% and 181% in these cases, where 2.5 bound acetyl groups per atom of active oxygen were used.

EXAMPLE XIX

25 A similar washing test to that described in Example VIII was carried out, using 9.95 parts of N-caproyldiacetamide instead of 5.96 parts of triacetamide and using 5.90 g of the corresponding mixture per litre instead of 5.70 g of mixture STrAA.

30 In this case, where 2.0 bound acetyl groups per atom of active oxygen were used, the relative improvement in the brightness of the washed material was 104%.

EXAMPLE XX

35 Each of three different detergent compositions A, B and C contained:

- 12% non-ionic detergent (isononylphenol-polyglycoether, containing about 8 ethylene oxide groups in each molecule) 40
- 36% sodium tripolyphosphate
- 8% sodium silicate, $\text{SiO}_2/\text{Na}_2\text{O}$ ratio = 2/1
- 2% commercial CMC, containing 50% sodium salt of carboxymethylcellulose 45
- 6.6% sodium perborate

Further these four compositions contained respectively:

- Composition A: 4.12% tetra-acetylhydrazine 50
- Composition B: 4.40% tetra-acetylmethylenediamine
- Composition C: no additional substances.

55 In all three compositions, the balance was sodium sulphate. In composition A and B, the ratio:

$$\frac{\text{bound acyl groups}}{\text{atom of active oxygen}} = 2.0$$

60 All the compositions were used in a concentration of 5.00 g/l for washing pieces of cotton fabric, which had been soiled uniformly with blackcurrant juice. After thoroughly rinsing with water and ironing, the brightness (or apparent luminosity) of the fabric was 49.4 (brightness of magnesium oxide = 100).

65 Pieces of this fabric were used for washing with the three detergent compositions A, B and C. After rinsing three times and ironing, their brightnesses are measured by means of a photo-electric tristimulus reflectometer. The results are shown in the following table. 70

| Temperature of treatment | Brightness of fabric pieces, washed and bleached in composition | | |
|--------------------------|---|------|------|
| | A | B | C |
| 60° | 68.1 | 68.2 | 60.4 |
| 50° | 72.2 | 72.5 | |
| 35° | 70.3 | 69.1 | |
| 18° | 66.3 | 67.5 | |

75 In the following table, the improvements in the brightness caused by the above-mentioned activators are expressed as percentages of the difference between the brightness of the fabric

after rinsing with water only and the brightness of the material after treatment with detergent composition C at 50° C., as compared with the brightness of the latter.

| Temperature of treatment | Percentage improvement of brightness. Treatment in composition | | |
|--------------------------|--|-----|---|
| | A | B | C |
| 60° | 70 | 71 | 0 |
| 50° | 107 | 110 | |
| 35° | 90 | 79 | |
| 18° | 54 | 65 | |

The same results are obtained if the detergent compositions contain fluorescent brighteners, dyestuffs and/or perfumes. Essentially the same results are obtained with other kinds of fabrics, such as wool, linen, silk, viscose rayon, acetate rayon, polyamide, polyester, polyacrylonitrile, polyvinyl and other natural and synthetic fibres. The same applies to the use of other non-ionic surface active agents and other builders.

EXAMPLE XXI

Pieces of unbleached cotton fabric were boiled for 3 hours in a 1% solution of sodium hydroxide in water which had been softened by means of a cation exchanger. Thereupon they were rinsed with softened water until the sodium hydroxide was almost completely eliminated. A sample of the treated fabric was dried (sample M) and the light remissivity (diffuse reflections) was measured with the aid of a photoelectric remission-meter. The brightness (G) was 75.9% and the tristimulus blue and amber remissivities (B and A) were respectively 65.6 and 78.8% of those of magnesium oxide freshly precipitated from the vapour phase.

The yellowness J was 17.1 according to the formula of R. S. Hunter ("Photoelectric tristimulus colorimetry with three filters," Circular of the National Bureau of Standards C 429, U.S. Government Printing Office, Washington, 1942, p. 22) :

$$J = \frac{A-B}{G} 100$$

The pieces of cotton fabric boiled with sodium hydroxide and rinsed with softened water were bleached for 15 minutes in the following ways:

a) at 60° C. with a solution containing 3.0 g of anhydrous soda and 2.0 g of sodium bicarbonate per litre and a quantity of hydrogen peroxide equivalent to an active oxygen content of 1.18 g per litre of solution. At 20° C. the pH of the solution was 10.0;

b) at 82° C. with a bleaching liquid of the same composition as that mentioned under a). At 20° C. the pH of this solution was 10.0;

c) at 60° C. with a bleaching liquid of the same composition as described under a) and b), but containing in addition 7.9 g of TAMD (tetra-acetylmethylenediamine) and 2.62 g of sodium hydroxide per litre. In this case, the ratio of bound acyl groups per atom of active oxygen, added to the bleaching liquid, was 2. At 20° C. the pH of this solution was 10.0. After the bleaching process, the pieces of cotton fabric were rinsed with softened water and dried.

Measurement with the photoelectric remission meter gave the following remission values:

| Bleaching treatment | Temp. °C. | Tristimulus-remission values | | | Yellowness J |
|---------------------|-----------|------------------------------|------|------|--------------|
| | | G | B | A | |
| a | 60° | 79.5 | 67.8 | 82.5 | 18.3 |
| b | 82° | 80.2 | 69.1 | 83.1 | 17.3 |
| c | 60° | 86.1 | 78.5 | 88.9 | 11.9 |

While with bleaching with hydrogen peroxide without TAMD the yellowness calculated according to the Hunter formula had hardly altered or had even increased somewhat, with bleaching in the presence of TAMD it decreased considerably. Expressed in percentages of the difference between the remission values of the piece of fabric bleached according to treatment *a* and those of the unbleached sample *M*, the improvements of the remission values of the treated materials, as compared with those of the fabric bleached according to treatment *a*, were:

Percentage improvements:

| Bleaching treatment | Temp. °C. | Tristimulus-remissivity values | | |
|---------------------|-----------|--------------------------------|------|------|
| | | G | B | A |
| a | 60° | 0 | 0 | 0 |
| b | 82° | 19% | 59% | 16% |
| c | 60° | 183% | 487% | 173% |

Consequently, the improvements caused by adding TAMD at 60° were 8 to 10 times as great as the improvements caused by increasing the temperature from 60° to 82° without TAMD.

The pieces of cotton fabric bleached according to method c) contained considerably less seedrests than the pieces bleached according to the methods a) and b). Moreover, the cotton bleached in the presence of TAMD at 60° C. was much more hydrophilic than both of the others. A drop of water put on it was absorbed immediately.

EXAMPLE XXII

A piece of unbleached cotton fabric was boiled for 1½ hours in a 1% solution of sodium hydroxide in water softened by means of a cation exchanger. Subsequently it was boiled another 1½ hours in another, fresh 1% solution of sodium hydroxide in softened water. Thereupon it was rinsed with softened water until the sodium hydroxide was almost completely eliminated. A sample of the treated cotton fabric was dried (sample N) and the light remissivity (diffuse reflections) was measured with the aid of a photo-electric remission meter. The brightness (G) and the tristimulus blue and amber remissions (B and A) were 79.4, 73.3 and 81.3 respectively. Consequently, the yellowness according to the formula of R. S. Hunter was 10.0.

Various parts of the piece of cotton fabric boiled with sodium hydroxide and rinsed with softened water were put into one of the following eight bleaching liquids, thereafter heated in 10 minutes from 20° to the temperature for treatment mentioned hereafter and subsequently kept at that temperature for 15 minutes. Then the pieces of cotton fabric were rinsed with softened water and dried; subsequently their light remissions were measured.

The compositions of the bleaching liquids, their temperatures and the results of the measurements are indicated in the following table:

| Composition of the bleaching liquid | | | | Temp. °C. | End pH | Tristimulus remission values | | | Yellow- ness | Percentage improve- ment of the | |
|--------------------------------------|--------------------------------|----------|----------|--------------|-----------|------------------------------------|------|------|-----------------|------------------------------------|----------------------|
| 30% H ₂ O ₂ | neutral water g/l (100%) | NaOH | TAMD | | | G | B | A | | bright- ness G | yellow- ness J |
| 10 ml/l | 0 | 0 | 0 | 50° | 8.0 | 82.2 | 75.4 | 83.4 | 9.6 | 0 | 0 |
| " | 0 | 0.53 g/l | 3.78 g/l | 50° | 5.1 | 85.9 | 80.7 | 86.0 | 6.1 | 132% | 875% |
| " | 2.14 g/l | 0 | 0 | 50° | 9.8 | 84.0 | 76.7 | 84.2 | 8.8 | 64% | 200% |
| " | 2.14 g/l | 3.18 g/l | 3.78 g/l | 50° | 9.6 | 86.7 | 82.3 | 86.6 | 4.9 | 161% | 1175% |
| " | 0 | 0 | 0 | 82° | 7.6 | 86.8 | 82.0 | 86.9 | 5.6 | 164% | 1000% |
| " | 0 | 0.98 g/l | 3.78 g/l | 82° | 5.0 | 88.0 | 84.6 | 88.0 | 3.9 | 207% | 1425% |
| " | 2.14 g/l | 0 | 0 | 82° | 9.7 | 86.6 | 81.6 | 86.8 | 6.0 | 157% | 900% |
| " | 2.14 g/l | 3.10 g/l | 3.78 g/l | 82° | 9.0 | 88.2 | 84.7 | 87.9 | 3.6 | 214% | 1500% |

meter, a woollen fabric gave the following light remission values: brightness (G) 72.3; tristimulus blue and amber remission (B and A) 57.7 and 74.8 respectively. Thus the yellowness (J) according to R. S. Hunter was 23.5. Two parts of this fabric were bleached for 45 minutes at 35° C. in water softened with the aid of a cation exchanger. Thereafter they were rinsed with softened water, dried and their light remission values were measured again.

fabric bleached in the presence of TAMD contain no seedstems, in contrast to the cotton pieces bleached without TAMD. In these tests, the ratio of bound acyl groups per atom of active oxygen present in the bleaching liquid was 0.75. The concentrations of active oxygen and TAMD may be chosen both higher and lower, whereby it is not necessary to adhere to the value 0.75 for the above-mentioned ratio.

EXAMPLE XXIII

On measuring with a photoelectric remission

The improvements as to the remission values and the yellowness of the bleached cotton fabrics are expressed in percentages of the difference between the corresponding values of the unbleached sample N and those of the piece of cotton fabric bleached without TAMD and without waterglass at 50° C. as compared with those of the latter.

The improvements due to the presence of TAMD in the bleaching liquid were most significant both at 82° C. and at 50° C. without and with waterglass. All pieces of cotton

| Composition of the bleaching liquid | bleaching treatment a | bleaching treatment b |
|---------------------------------------|-------------------------|-------------------------|
| Hydrogen peroxide | 1.412 g active oxygen/l | 1.412 g active oxygen/l |
| TAMD | 0 | 9.44 g/l |
| NaOH | 0 | 3.12 g/l |
| End pH | 9.6 | 8.1 |
| brightness | 75.0 | 77.5 |
| tristimulus blue remission | 60.9 | 63.9 |
| tristimulus amber remission | 77.1 | 90.0 |
| yellowness | 21.3 | 20.5 |
| Improvement by TAMD in the brightness | 0 | 93% |
| tristimulus blue remission | 0 | 94% |
| tristimulus amber remission | 0 | 96% |
| yellowness | 0 | 36% |

The improvements of the remission values and the yellowness are again expressed as percentages of the difference between the corresponding values of the unbleached fabric and those of the fabric bleached according to treatment a, as compared with those of the latter.

By using TAMD in the bleaching liquid, the woollen fabric was therefore clearly bleached better.

The concentrations of active oxygen and TAMD may be chosen both higher and lower, whereby it is not necessary to adhere to the ratio between the active oxygen and activator concentrations given above.

Instead of hydrogen peroxide in the Examples XXI—XXIII, other compounds releasing active oxygen may also be used, such as perborate, percarbonate and pyrophosphate-perhydrate. Instead of TAMD, other activating agents according to the invention may also be used. The duration of the bleaching treatment may be chosen in dependence upon the bleaching and activating agent concentrations, the temperature, the pH of the bleaching liquid and the improvement required. If desired, a surface active substance may be added so as to accelerate wetting of the fabric.

EXAMPLE XXIV

Pieces of cotton fabric soiled with the juice of blackcurrants as described in Example I were treated according to one of the following

three processes:

A) Washing for 10 minutes at 50° C. in suds containing:

| | |
|---------------------------|----------|
| sodium soap | 1.00 g/l |
| sodium CMC (100%) | 0.10 g/l |
| sodium carbonate anh. | 3.86 g/l |
| neutral waterglass (100%) | 0.36 g/l |

After washing, the material was rinsed twice with water, first for 10 minutes at 50° C., subsequently for 3 minutes at 20° C.

B) Washing and bleaching for 10 minutes at different temperatures in suds of the same composition as described under a), but containing in addition:

| | |
|------------------------------|-----------|
| sodium perborate | |
| (10.2% active oxygen) | 0.500 g/l |
| tetra-acetylmethylenediamine | 0.335 g/l |

After washing and bleaching, the material was rinsed twice with water, first for 10 minutes at the same temperature at which washing and bleaching took place, subsequently for 3 minutes at 20° C.

C) Washing for 10 minutes at different temperatures in suds of the same composition as described under A), followed by rinsing and bleaching simultaneously for 10 minutes at the washing temperature with water containing:

sodium perborate
(10.2% active oxygen) 0.500 g/l
tetra-acetylmethylenediamine 0.335 g/l

After this treatment, the material was rinsed for 3 minutes at 20° C.

The brightness of the treated material is mentioned in the following table:

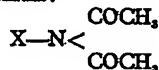
| Process | A | | B | | C | | |
|---|----|----|----|----|----|----|----|
| Temperature of test in °C. | 50 | 35 | 50 | 60 | 35 | 50 | 60 |
| Brightness of treated material in units | 58 | 65 | 70 | 68 | 66 | 73 | 75 |
| Brightness of magnesium oxide = 100 units | | | | | | | |

WHAT WE CLAIM IS:—

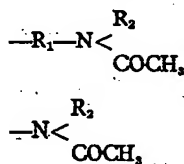
1. A process for preparing a washing and/or bleaching composition, which comprises adding to an inorganic peroxy compound an activator therefor comprising at least one compound containing one or more nitrogen atoms and having at least two acyl groups attached to the same nitrogen atom.

2. A process according to claim 1, in which the activator comprises at least one compound selected from N-diacylated amines, N-diacylated ammonia, N-diacylated amides, N-diacylated urethanes, N-diacylated hydrazines and N-diacylated alkylene diamines.

3. A process according to claim 1, in which the activator is one or more compounds having the general formula:



in which X represents a phenyl radical, an acyl group derived from a lower aliphatic mono-carboxylic acid, as hereinbefore defined, or a lower alkyl radical as hereinbefore defined



- 35 group, in which R₁ represents a lower alkylene group as hereinbefore defined and R₂ represents hydrogen or an acetyl group.

4. A process according to claim 1, 2 or 3, for preparing a dry, stable bleaching composition in which the peroxy compound is sodium perborate.

5. A process according to claim 1, 2, 3 or 4, in which the activator is N,N,N',N'-tetraacetylmethylenediamine and/or N,N,N',N'-tetraacetylmethylenediamine.

6. A process according to any preceding claim, in which the activator is added in an

amount corresponding to 0.5 to 4.0 bound acyl groups per atom of active oxygen.

7. A process for preparing a washing and/or bleaching composition according to claim 1, as described with reference to the foregoing Examples.

8. A process for washing and/or bleaching textile products, which comprises effecting washing and/or bleaching with the aid of a liquid containing an inorganic peroxy compound and an activator therefor comprising one or more compounds containing one or more nitrogen atoms and having at least two acyl groups attached to the same nitrogen atom.

9. A process according to claim 8, in which washing and/or bleaching is effected at a temperature lower than the boiling temperature.

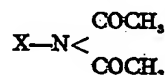
10. A process according to claim 9, in which washing and/or bleaching is effected at a temperature of 15°—85° C.

11. A process for washing and/or bleaching textile products according to claim 8, as described with reference to the foregoing Examples.

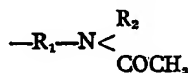
12. A washing and/or bleaching composition comprising an inorganic peroxy compound and an activator therefor comprising at least one compound containing one or more nitrogen atoms having at least two acyl groups attached to the same nitrogen atom.

13. A washing and/or bleaching composition as claimed in claim 12, in which the activator comprises at least one compound selected from N-diacylated amines, N-diacylated ammonia, N-diacylated amides, N-diacylated urethanes, N-diacylated hydrazines and N-diacylated alkylene diamines.

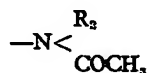
14. A washing and/or bleaching composition as claimed in claim 12, in which the activator comprises one or more compounds having the general formula:



in which X represents a phenyl radical, an acyl group derived from a lower aliphatic mono-carboxylic acid as hereinbefore defined, a lower alkyl radical as hereinbefore defined or a



or



group, in which R_1 represents a lower alkylene group as hereinbefore defined and R_2 represents hydrogen or an acetyl group.

15. A washing and/or bleaching composition as claimed in claim 12, in which the activator comprises tripropionylhydrazine.

16. A washing and/or bleaching composition as claimed in claim 13, in which the activator comprises diacetamide.

17. A washing and/or bleaching composition as claimed in claim 14, in which the activator comprises N,N,N',N' -tetra-acetyl-methylenediamine.

18. A washing and/or bleaching composition as claimed in claim 14, in which the activator comprises tetraacetylhydrazine.

19. A washing and/or bleaching composition as claimed in claim 14, in which the activator comprises triacetylhydrazine.

20. A washing and/or bleaching composition as claimed in claim 14, in which the activator comprises triacetamide.

21. A washing and/or bleaching composition

as claimed in claim 14, in which the activator comprises diacetylpropylamine.

22. A washing and/or bleaching composition as claimed in claim 14, in which the activator comprises diacetanilide.

23. A washing and/or bleaching composition as claimed in claim 14, in which the activator comprises N,N,N',N' -tetraacetyl-ethylenediamine.

24. A washing and/or bleaching composition as claimed in claim 14, in which the activator comprises N,N,N' -triacetyl-methylene-diamine.

25. A washing and/or bleaching composition as claimed in any of claims 12 to 24, in which the activator is added in an amount corresponding to 0.5—4.0 bound acyl groups per atom of active oxygen.

26. A washing and/or bleaching composition as claimed in any of claims 12 to 25, in which the inorganic peroxy compound is selected from inorganic persalts, hydrogen peroxide and sodium peroxide.

27. A washing and/or bleaching composition as claimed in claim 26, in which the active oxygen releasing compound is sodium perborate.

28. A washing and/or bleaching composition according to claim 12, substantially as hereinbefore described with reference to the foregoing Examples.

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PROVISIONAL SPECIFICATION

No. 21220 A.D. 1959

Improvements in or relating to Washing and/or Bleaching Compositions

We, KONINKLIJKE INDUSTRIËLE MAATSCHAPPIJ VOORHEEN NOURY & VAN DER LANDE N.V., of 13 Brink, Deventer, The Netherlands, a company organised and existing under the laws of the Kingdom of the Netherlands, do hereby declare this invention to be described in the following statement:—

The invention relates to washing and/or bleaching agents containing an active oxygen releasing compound, for natural and/or synthetic fibres as well as for products manufactured therefrom or therewith, to a process for the preparation of such agents and to a process for washing and/or bleaching natural and/or synthetic fibres and products manufactured therefrom or therewith.

It is a well-known fact that on washing and/or bleaching natural and/or synthetic fibres, as well as textiles manufactured therefrom or therewith, use is made of agents containing, i.e., active oxygen releasing com-

pounds, which have a cleaning and/or bleaching action on natural and/or synthetic fibres and on products manufactured therewith or therefrom. As the active oxygen releasing compounds, inorganic-persalts, such as perborates, percarbonates, perphosphates, persulfates, persulphates and, moreover, hydrogen peroxide and sodium peroxide are used.

However, washing and/or bleaching agents containing such active oxygen releasing compounds generally have the disadvantage that their bleaching effect is relatively low at temperatures of 40—70° C., which gives rise to difficulties when these products are used in domestic machines in which the temperature of the wash-water is not higher than about 70° C.

It has now been found that, if an organic or inorganic compound containing at least one nitrogen atom to which at least two acyl groups are attached or mixtures thereof is added to

a washing and/or bleaching agent containing an active oxygen releasing compound, a product is obtained which is extraordinarily suitable for a washing and/or bleaching treatment of natural and/or synthetic fibres and of textiles manufactured therefrom or therewith at a temperature of 40—70° C.

It has already been proposed to enhance the bleaching effect of a washing agent containing an active oxygen releasing compound by adding thereto particular substances, so-called "activators." Definite quantities of organic acid anhydrides, for instance, have been added to washing agents containing perborates. However, in practice, this measure does not yield the desired result, as the reactivity of most acid anhydrides appears to be insufficient in this respect. Moreover, it has not been found possible to mix anhydrides with the other components of the washing agent in a simple manner.

It has also been proposed to add formamide and representatives of the nitrile group to washing agents containing active oxygen releasing compounds. However, formamide is a liquid and it is difficult to incorporate it into a pulverulent washing agent. The result obtained by adding nitriles is very small as well.

According to the invention, compounds having at least two acyl groups attached to one nitrogen atom are added to washing and/or bleaching agents containing an active oxygen releasing compound. Examples of these compounds are acylated mono- and polyamines containing at least one N-atom to which two acyl groups are attached, such as tetra-acetyl-ethylenediamine, diacetylbutylamine and diacetyl aniline; acid amides (i.e. ammonia of which 2 or 3 hydrogen atoms are replaced by acyl groups), e.g. dipropionamide, triacetamide,

N-acetyl-succinimide, N-acetyl-phthalimide and formyl acetamide; acylated hydrazines or derivatives thereof containing at least one N-atom to which 2 acyl groups are attached, e.g. tripropionyl hydrazine, tetra-acetyl hydrazine and tetrabenzoyl hydrazine; N-acyl-compounds, containing at least one N-atom to which 2 acyl groups are attached, derived from urethanes, semicarbazide, thiosemicarbazide and dicyanodiamide and derivatives of these compounds.

The washing and/or bleaching of natural and/or synthetic fibres or of products manufactured therefrom or therewith may take place by effecting the washing and/or bleaching treatment with the finished agents obtained according to the invention.

It is also possible, however, to effect the treatment with suds containing an active oxygen releasing compound to which an organic or inorganic compound containing at least one nitrogen atom to which at least two acyl groups are attached, or mixtures thereof, is added.

In both cases, very good results are obtained at a temperature of 40—70° C.

Hereafter, the invention will be further illustrated on the basis of some Examples.

EXAMPLE I

Pieces of cotton fabric were stained with the juice of blackcurrants, by evenly applying to them 2.7 cc. of blackcurrant juice per 100 cm² of surface of cotton fabric by means of a brush. After being dried in the air, the brightness of the fabric was measured with a photoelectric remission meter. It was 29% of the brightness of magnesium oxide.

Part of the pieces of material was washed for 15 minutes at 60° in suds of the following composition:

| | |
|---|----------|
| Sodium salt of dodecyl benzene sulphonic acid | 0.85 g/l |
| Lauryl isopropanolamide | 0.10 g/l |
| Tetrasodium pyrophosphate | 0.75 g/l |
| Pentasodium tripolyphosphate | 0.60 g/l |
| Alkaline water-glass ($\text{Na}_2\text{O}/\text{SiO}_2 = \frac{1}{2}$) | 0.20 g/l |
| Na CMC (100%) | 0.04 g/l |
| Sodium sulphate | 0.80 g/l |
| Sodium perborate (10.2% active oxygen) | 0.50 g/l |

With the exception of the sodium perborate, all concentrations refer to the anhydrous substances.

The percentage of brightness of the washed

pieces of material amounted to 64 (brightness of magnesium oxide = 100 units), which is 13 units higher than the percentage of brightness of the pieces of material after thorough wash-

ing with water, which was 51.

Another part of the material was washed in suds of the same composition, to which respectively 0.1, 0.4 and 0.5 g/l of tetra-acetyl hydrazine was added. These suds contained per atom of active oxygen from the perborate 0.63, 2.50 and 3.14 acetyl groups as tetra-acetyl hydrazine, respectively.

The percentages of brightness of the thus washed material were respectively 20, 31 and 34 units higher than the percentage of bright-

ness of the material which was only thoroughly washed with water. The relative improvements by adding tetra-acetyl hydrazine in the concentrations mentioned were therefore 54%, 138% and 162%.

EXAMPLE II

Pieces of the same kind of fabric, stained with blackcurrant juice, as used in Example I, were washed for 15 minutes at 60° C. in suds of the following composition:

| | |
|--|----------|
| Sodium soap | 3.1 g/l |
| Sodium carbonate | 1.00 g/l |
| Neutral water-glass ($\text{Na}_2\text{O}/\text{SiO}_2 = 1/3.3$) | 0.17 g/l |
| Sodium perborate (9.9% of active oxygen) | 0.68 g/l |

With the exception of the sodium perborate, all concentrations given refer to the anhydrous substances.

The percentage of brightness of the material was increased to 62% by washing (brightness of magnesium oxide=100 units); this is 11 units higher than the brightness obtained by only washing the material thoroughly with water.

If the suds also contained 0.42 g/l of tetra-acetyl hydrazine, the percentage of brightness of the material was increased to 73, which is

22 units more than the percentage of brightness obtained after thoroughly washing with water only. The relative improvement by adding tetra-acetyl hydrazine therefore amounted to 100%. In this case, the number of acetyl groups added to the suds as tetra-acetyl hydrazine was 2.0 per atom of active oxygen from the perborate.

EXAMPLE III

A detergent in powder form had the following composition:

| |
|--|
| 20.0% of sodium salt of dodecyl-(tetrapropylene)-benzene sulphonic acid |
| 26.0% of tetrasodium pyrophosphate |
| 16.0% of pentasodium tripolyphosphate |
| 4.8% of neutral water-glass ($\text{Na}_2\text{O}/\text{SiO}_2 = 1/3.3$) |
| 2.0% of sodium salt of carboxymethylcellulose |
| 27.6% of sodium sulphate |
| 13.6% of water |
| 100% |

100 parts by weight of this powder were mixed with 8 parts by weight of sodium perborate-tetrahydrate and 6.25 parts by weight of tetra-acetyl hydrazine (STAH mixture).

A solution was prepared, containing 5.70 g/l of the STAH mixture and pieces of the same kind of material stained with fruit juice,

as used in Example I, were washed in this solution for 15 minutes at 60° C.

The material was then rinsed three times, ironed with a hot iron and the brightness was measured with a Hunter photo-electric remission meter.

Besides this test, a similar test was carried out with a mixture of 100 parts by weight of

the afore-mentioned powder and 8 parts by weight of sodium perborate-tetrahydrate without tetra-acetyl hydrazine (mixture SO). 5.4 grams per litre solution were used of this mixture.

The brightness of the material washed with the STAH mixture was 27 units higher than the brightness of material thoroughly rinsed with water only (51 units).

In the case of the SO mixture, this difference in brightness was 12 units (brightness of magnesium oxide = 100 units).

So by using a quantity of tetra-acetyl hydrazine such as to correspond to 2.5 bound acetyl groups per atom of active oxygen, a relative improvement of 125% was obtained.

EXAMPLE IV

100 parts by weight of the detergent, as described in Example III, was mixed with 8 parts of sodium perborate-tetrahydrate and 6.60 parts of triacetyl hydrazine (STrAH mixture).

A solution was prepared containing 5.75 g per litre of this STrAH mixture and the same washing test was carried out with it as described in Example III.

The brightness of the material appears to be 22 units higher than the brightness of the material rinsed with water thoroughly (51 units). In the case of the SO mixture, this difference in brightness was 12 units.

So the relative improvement in this case, where 2.5 bound acetyl groups per atom of active oxygen were used, was 83%.

EXAMPLE V

100 parts by weight of the powder described in Example III were mixed with 8 parts of sodium perborate-tetrahydrate and 11.0 parts of tripropionyl hydrazine (STrPrH mixture).

A solution was prepared, containing 5.95 g per litre of this STrPrH mixture and a similar washing test was carried out with it as described in Example III, except that in this case the experiment was carried out at 50° C.

The brightness of the washed material appeared to be 23 units higher than the brightness of material washed thoroughly with water (51 units). In the case of the SO mixture, this difference in brightness was 12 units.

So the relative improvement in this case, where 3.3 bound propionyl groups per atom of active oxygen were used, was 92%.

EXAMPLE VI

100 parts by weight of the powder described in Example III were mixed with 8 parts of sodium perborate-tetrahydrate and 7.05 parts of tetra-acetylenediamine (STAED mixture).

A solution was prepared, containing 5.75 g per litre of this STAED mixture and a similar washing test was carried out with it as described in Example III, except that another lot of cotton fabric, stained with blackcurrant juice, was used.

The brightness of the washed material ap-

peared to be 23 units higher than the brightness of material washed thoroughly with water (51 units). In the case of the SO mixture, this difference in brightness was 13 units.

So the relative improvement in this case, where 2.5 bound acetyl groups per atom of active oxygen were used, was 77%.

EXAMPLE VII

100 parts by weight of the powder described in Example III were mixed with 8 parts of sodium perborate-tetrahydrate and 6.31 parts of diacetamide (SDAA mixture).

A solution was prepared, containing 5.72 g per litre of this SDAA mixture and a similar washing test was carried out with it as described in Example VI.

The brightness of the washed material appeared to be 22 units higher than the brightness of material washed thoroughly with water (51 units). In the case of the SO mixture, this difference in brightness was 13 units.

So the relative improvement in this case, where 2.5 bound acetyl groups per atom of active oxygen were used, was 69%.

EXAMPLE VIII

100 parts by weight of the powder described in Example III were mixed with 8 parts of sodium perborate-tetrahydrate and 5.96 parts of triacetamide (STrAA mixture).

A solution was prepared containing 5.70 g per litre of this STrAA mixture and a similar washing test was carried out with it as described in Example VI.

The brightness of the washed material appeared to be 30 units higher than the brightness of material washed thoroughly with water (51 units). In the case of the SO mixture, this difference in brightness was 13 units.

So the relative improvement in this case, where 2.5 bound acetyl groups per atom of active oxygen were used, was 131%.

EXAMPLE IX

A detergent in powder form had the following composition:

| | |
|---------------------------|-----|
| 43% of sodium soap | 110 |
| 25% of sodium carbonate | |
| 3% of neutral water-glass | |
| 29% of water | |

100%

100 parts by weight of this powder were mixed with 7.5 parts by weight of sodium perborate-tetraborate and 6.70 parts by weight of diacetylpropylamide (ZDAPrA mixture).

A solution was prepared containing 9.14 g per litre of this ZDAPrA mixture and pieces of the same kind of material stained with fruit juice, as used in Example I, were washed in this solution for 15 minutes at 50° C.

The material was then rinsed three times, ironed with a hot iron and the brightness was measured with a Hunter photo-electric remission meter.

Besides this test, a similar test was carried out with a mixture of 100 parts by weight of the afore-mentioned powder and 7.5 parts by weight of sodium perborate-tetrahydrate without diacetyl propylamide (ZO mixture). 8.60 grams per litre of this mixture were used.

The brightness of the material washed with the ZDAPrA mixture was 19 units higher than the brightness of material thoroughly rinsed with water only (51 units).

In the case of the Zo mixture, this difference in brightness was 12 units (brightness of magnesium oxide = 100 units).

So by using a quantity of diacetyl propylamine such as to correspond to 2.0 bound acetyl groups per atom of active oxygen, a relative improvement of 58% was obtained.

The invention is not limited to the Examples given, as variations are possible within the scope of the invention.

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PROVISIONAL SPECIFICATION No. 26061 A.D. 1959

Improvements in or relating to Washing and/or Bleaching Compositions

We, KONINKLIJKE INDUSTRIEEL MAATSCHAPPIJ VOORHEEN NOURY & VAN DER LANDE N.V., of 13 Brink, Deventer, The Netherlands, a company organised and existing under the laws of the Kingdom of the Netherlands, do hereby declare this invention to be described in the following statement:—

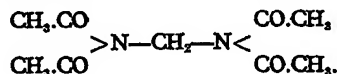
The present invention relates to washing and/or bleaching agents containing an active oxygen releasing compound and is concerned particularly, but not exclusively, with the invention disclosed in co-pending Application No. 21220/59.

As described in the aforesaid application, it has been found that, if an organic or inorganic compound containing at least one nitrogen atom to which at least two acyl groups are attached or a mixture thereof is added to a washing and/or bleaching agent containing an active oxygen releasing compound, a product is obtained which is extraordinarily suitable for a washing and/or bleaching treatment of natural and/or synthetic fibres and of textiles manufactured therefrom or therewith at a temperature of 40° C.—70° C.

The acyl compounds disclosed in the aforesaid application include acylated mono- and polyamines, acid amides, acylated hydrazines and their derivatives and many N-acyl compounds derived, for example, from urethanes.

The present invention provides a new acyl compound, which is eminently suitable for use in washing and/or bleaching agents of the kind disclosed in the aforesaid application.

Accordingly, the present invention consists in N,N'-tetra-acetyl-methylene diamine. This compound has the structure:



The present invention also consists in a method of preparation of N,N'-tetra-acetyl-

methylene-diamine, which comprises acetylating N,N'-di-acetyl-methylene-diamine. In accordance with a preferred embodiment of this aspect of the invention, N,N'-tetra-acetyl-methylene-diamine (hereinafter referred to as "TAMD") is prepared by a method in which ketene is used as an acetylation agent.

The invention further consists in (1) a washing and/or bleaching agent containing an active oxygen releasing compound and TAMD, (2) a method of washing and/or bleaching using such an agent, and (3) a method of washing and/or bleaching, in which TAMD is added to suds containing an active oxygen releasing compound.

It has been found that TAMD, which is a new chemical substance and which falls within the requirements of the aforesaid application, having 2 nitrogen atoms to each of which 2 acyl groups are attached, is most suitable for enhancing the bleaching effect at lower temperatures of a washing agent containing an active oxygen releasing compound. Moreover, TAMD comes into special consideration for practical application, because this substance can be manufactured in a relatively cheap way.

EXAMPLES.

EXAMPLE I.

Pieces of cotton fabric were stained with the juice of blackcurrants; by evenly applying to them 2.7 cc of blackcurrant juice per 100 cm² of surface cotton fabric by means of a brush. After drying in the air, rinsing thoroughly with water and drying again, the brightness of the pieces of fabric, measured with a photo-electric remission meter, was 53% of the brightness of magnesium oxide freshly condensed from the atmosphere.

Seven lots of these pieces of material were washed for 10 minutes at 60° C. in seven different suds.

All these suds contained:

| | |
|---|-----------|
| Sodium salt of dodecyl benzene sulphonic acid | 0.85 g/l |
| Lauryl isopropanolamide | 0.10 g/l |
| Tetrasodium pyrophosphate | 0.75 g/l |
| Pentasodium tripolyphosphate | 0.60 g/l |
| Alkaline water-glass ($\text{Na}_2\text{O}/\text{SiO}_2 = \frac{1}{2}$) | 0.20 g/l |
| NaCMC (100%) | 0.040 g/l |
| Sodium sulphate | 0.80 g/l |

All concentrations refer to the anhydrous substances.

Further components of the different suds were as follows:

| | | |
|---------|--|----------|
| Suds 1: | sodium perborate (10.0% active oxygen) | 0.52 g/l |
| Suds 2: | sodium perborate | 0.50 g/l |
| | TAMD | 0.40 g/l |
| | ratio $\frac{\text{bound acetyl groups}}{\text{atoms active oxygen}} = 2.4$ | |
| Suds 3: | sodium perborate | 0.40 g/l |
| | TAMD | 0.40 g/l |
| | ratio $\frac{\text{bound acetyl groups}}{\text{atoms active oxygen}} = 3.0$ | |
| Suds 4: | sodium perborate | 0.40 g/l |
| | TAMD | 0.30 g/l |
| | ratio $\frac{\text{bound acetyl groups}}{\text{atoms active oxygen}} = 2.25$ | |
| Suds 5: | sodium perborate | 0.30 g/l |
| | TAMD | 0.40 g/l |
| | ratio $\frac{\text{bound acetyl groups}}{\text{atoms active oxygen}} = 4.0$ | |
| Suds 6: | sodium perborate | 0.30 g/l |
| | TAMD | 0.30 g/l |
| | ratio $\frac{\text{bound acetyl groups}}{\text{atoms active oxygen}} = 3.0$ | |
| Suds 7: | sodium perborate | 0.20 g/l |
| | TAMD | 0.30 g/l |
| | ratio $\frac{\text{bound acetyl groups}}{\text{atoms active oxygen}} = 4.4$ | |

After washing, rinsing and drying, the brightness of the pieces of material was measured.

The results were:

| Suds No. | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|---|----|------|------|------|------|------|------|
| Brightness (% of MgO) | 62 | 81 | 79 | 79 | 76 | 76 | 71.5 |
| Difference with the washing-test without TAMD | 0 | 19 | 17 | 17 | 14 | 14 | 9.5 |
| Relative improvement | 0 | 210% | 190% | 190% | 155% | 155% | 105% |

The relative improvement is expressed as percentages of the difference in brightness between the pieces of material washed with 0.52 g/l perborate without TAMD, and the pieces of material only rinsed with water (brightness 53).

In spite of the very considerable decrease in perborate content of some of the suds, great improvements in bleaching effect were obtained when TAMD was added to the suds.

EXAMPLE II.

A detergent in powder form was made up having the following composition:

50% of sodium soap,
16% of sodium carbonate,
3% of neutral water-glass,
31% of water.

Subsequently five minutes were prepared, namely:

Mixture 1: 90 parts by weight of above-mentioned detergent
10 parts by weight of sodium perborate (9.7% active oxygen)

Mixture 2: 85.9 parts by weight of above-mentioned detergent
8.6 parts by weight of sodium perborate
5.5 parts by weight of TAMD

$$\text{ratio} \frac{\text{bound acyl groups}}{\text{atoms active oxygen}} = 2.0$$

Mixture 3: 87.1 parts by weight of above-mentioned detergent
8.7 parts by weight of sodium perborate
4.2 parts by weight of TAMD

$$\text{ratio} \frac{\text{bound acyl groups}}{\text{atoms active oxygen}} = 1.5$$

Mixture 4: 88.5 parts by weight of above-mentioned detergent
5.8 parts by weight of sodium perborate
5.7 parts by weight of TAMD

$$\text{ratio} \frac{\text{bound acyl groups}}{\text{atoms active oxygen}} = 3.0$$

Mixture 5: 91.0 parts by weight of above-mentioned detergent
 4.6 parts by weight of sodium perborate
 4.4 parts by weight of TAMD

$$\text{ratio} \frac{\text{bound acyl groups}}{\text{atoms active oxygen}} = 3.0$$

These mixtures were used in concentrations of 6.9; 7.2; 7.1; 7.0 and 6.8 g/l respectively.

In this way, the following concentrations were obtained (in g/l)

| Mixture No. | 1 | 2 | 3 | 4 | 5 |
|---------------------|------|------|------|------|------|
| Sodium soap | 3.1 | 3.1 | 3.1 | 3.1 | 3.1 |
| Sodium carbonate | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 |
| Neutral water-glass | 0.19 | 0.19 | 0.19 | 0.19 | 0.19 |
| Sodium perborate | 0.69 | 0.62 | 0.62 | 0.41 | 0.31 |
| TAMD | 0 | 0.40 | 0.30 | 0.40 | 0.30 |

Five lots of pieces of cotton material, stained with the same blackcurrant juice as in Example I, were washed in these suds for 10 minutes at 60° C. After washing, rinsing and drying, the brightness of the pieces of material was measured, which gave the following results:

| Mixture No. | 1 | 2 | 3 | 4 | 5 |
|---|------|------|------|-----|------|
| Brightness (% of MgO) | 62.5 | 75 | 66.5 | 70 | 65.5 |
| Difference with the washing-test without TAMD | 0 | 12.5 | 4.0 | 7.5 | 3.0 |
| Relative improvement | 0 | 208 | 67 | 125 | 50 |

- 10 The relative improvement is expressed as percentages of the difference in brightness between the pieces of material washed with 0.69 g/l of perborate without TAMD (mixture 1) and the pieces of material only rinsed with water (brightness 56.5).
- 15 In spite of the very considerable decrease in perborate content of some of the suds, great improvements in bleaching effect were obtained when TAMD was added to the suds.

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PROVISIONAL SPECIFICATION No. 34695 A.D. 1959

Improvements in or relating to Washing and/or Bleaching Compositions

- 20 We, KONINKLIJKE INDUSTRIËLE MAAT- LANDE N.V., of 13 Brink, Deventer, The
 SCHAPPIJ VOORHEEN NOURY & VAN DER Netherlands, a company organised and exist-

ing under the laws of the Kingdom of the Netherlands, do hereby declare this invention to be described in the following statement:—

5 The present invention relates to washing and/or bleaching agents containing an active oxygen releasing compound and is concerned particularly with the invention disclosed in co-
pending Applications Nos. 21220/59 and 26061/59.

10 It is disclosed in Application No. 21220/59 that, if an organic or inorganic compound containing at least one nitrogen atom to which at least two acyl groups are attached or a mixture thereof is added to a washing and/or
15 bleaching agent containing an active oxygen releasing compound, a product is obtained which is extraordinarily suitable for a washing and/or bleaching treatment of natural and/or synthetic fibres and of textiles manufactured
20 therefrom or therewith at a temperature of 40°—70° C. Application No. 26061/59 discloses a novel compound, N,N'-tetra-acetyl-
25 methylene-diamine, which is eminently suitable for use in washing and/or bleaching agents of the kind disclosed in Application No. 21220/59. The use in this way of N,N'-tetra-

acetyl-methylene-diamine (referred to hereinafter as "TAMD") is illustrated in Application No. 26061/59 in a number of Examples in conjunction with sodium perborate as the
30 active oxygen releasing compound and it has been found that excellent results are given by washing and/or bleaching compositions containing TAMD and other percompounds, as illustrated in the following Examples: 35

EXAMPLE I

Pieces of cotton fabric were stained with the juice of blackcurrants, by evenly applying to them 2.7 cc of household blackcurrant juice per 100 cm² of surface of cotton fabric by
40 means of a brush. After drying in the air, rinsing thoroughly with water and drying again, the brightness of the pieces of fabric, measured with a photo-electric remission meter, was 52.5% of the brightness of mag-
45 nesium oxide freshly condensed from the atmosphere.

Two lots of these pieces of material were washed for 10 minutes at 60° C. in four different suds, prepared in the following way: 50

A detergent was made up having the following composition:

| | |
|---|-------|
| Sodium salt of dodecyl benzene sulphonic acid | 22.4% |
| Lauryl isopropanolamide | 2.6% |
| Tetrasodium pyrophosphate | 20.0% |
| Pentasodium tripolyphosphate | 15.8% |
| Alkaline water-glass ($\text{Na}_2\text{O}/\text{SiO}_2 = \frac{1}{2}$) | 5.1% |
| Sodium carboxymethylcellulose (NaCMC) (100%) | 1.0% |
| Sodium sulphate | 21.0% |
| Water | 12.1% |

Subsequently four mixtures were prepared, namely:

- Mixture 1: 85.5 parts by weight of above-mentioned detergent;
14.5 parts by weight of sodium pyrophosphate perhydrate
(8.05% active oxygen)
- Mixture 2: 77.9 parts by weight of above-mentioned detergent;
13.2 parts by weight of sodium pyrophosphate perhydrate;
8.9 parts by weight of TAMD
- Mixture 3: 91.2 parts by weight of above-mentioned detergent;
8.8 parts by weight of sodium percarbonate
(14.6% active oxygen)
- Mixture 4: 82.7 parts by weight of above-mentioned detergent;
7.8 parts by weight of sodium percarbonate;
9.5 parts by weight of TAMD

These mixtures were used in concentrations of 4.45, 4.88, 4.16 and 4.59 g/l respectively. To each of the suds, a quantity of oxygen bleaching agent was added which corresponded to 52 mg/l of active oxygen.

5

All suds contained the components of the original detergent in the same concentrations. For the TAMD-containing mixtures 2 and 4, the ratio was:

$$\frac{\text{bound atoms} \quad \text{acyl groups}}{\text{active oxygen}} = 2.5$$

10

After washing, rinsing and drying, the brightness of the pieces of material was measured. The results were:

| Mixture No. | 1 | 2 | 3 | 4 |
|---|--------------------------|--------------------------|--------------|--------------|
| Oxygen releasing substance | pyrophosphate perhydrate | pyrophosphate perhydrate | percarbonate | percarbonate |
| Addition | — | TAMD | — | TAMD |
| Brightness (% of MgO) | 62 | 80 | 61 | 79 |
| Difference with the washing-test without TAMD | 0 | 18 | 0 | 18 |
| Relative improvement | 0 | 190% | 0 | 212% |

15 The relative improvement caused by TAMD is expressed as a percentage of the difference in brightness between the pieces of material washed with the mixture containing the same oxygen bleaching agent without TAMD, and
20 the pieces of material only rinsed with water (brightness 52.5).

EXAMPLE II

A detergent in powder form had the following composition:

50.7% of sodium soap
16.1% of sodium carbonate
2.8% of neutral water-glass
30.4% of water

25

Subsequently four mixtures were prepared, namely:

30

- 30
- Mixture 1: 88 parts by weight of above-mentioned detergent;
12 parts by weight of sodium pyrophosphate perhydrate (8.1% active oxygen)
- Mixture 2: 82.6 parts by weight of above-mentioned detergent;
11.3 parts by weight of sodium pyrophosphate perhydrate;
6.1 parts by weight of TAMD
- Mixture 3: 93 parts by weight of above-mentioned detergent;
7 parts by weight of sodium percarbonate (14.6% active oxygen)
- Mixture 4: 87 parts by weight of above-mentioned detergent;
6.6 parts by weight of sodium percarbonate;
6.4 parts by weight of TAMD

For the TAMD-containing mixtures 2 and 4, the ratio was:

$$\frac{\text{bound acyl groups}}{\text{atoms active oxygen}} = 2.0$$

These mixtures were used in concentrations of 6.9, 7.35, 6.53 and 6.98 g/l respectively. To each of the suds, a quantity of oxygen bleaching agent was added which corresponded

to 67 mg/l active oxygen.

All suds contained the components of the original detergent in the same concentrations.

Four lots of pieces of cotton material stained with the same black currant juice as described in Example I were washed in these suds for 10 minutes at 60° C. After washing, rinsing and drying, the brightness of the pieces of material was measured, which gave the following results:

| Mixture No. | 1 | 2 | 3 | 4 |
|---|--------------------------|--------------------------|--------------|--------------|
| Oxygen releasing substance | pyrophosphate perhydrate | pyrophosphate perhydrate | percarbonate | percarbonate |
| Addition | — | TAMD | — | TAMD |
| Brightness (% of MgO) | 62 | 78 | 60.5 | 73 |
| Difference with the washing-test without TAMD | 0 | 16 | 0 | 12 |
| Relative improvement | 0 | 200% | 0 | 192% |

The relative improvement caused by TAMD is expressed as percentages of the difference in brightness between the pieces of material washed with the mixture containing the same oxygen bleaching agent without TAMD, and the pieces of material only rinsed with water

(brightness 54).

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